

ENCLOSURE (B) 7

STUDIES ON THE MANUFACTURE
OF AVIATION GASOLINE BY HIGH PRESSURE
HYDROCRACKING OF PINE ROOT OIL

by

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ENCLOSURE (B)7

LIST OF TABLES
AND ILLUSTRATIONS

Table I(B)7	Results of Autoclave Tests at 100 kg/cm ²	Page 105
Table II(B)7	Results of Autoclave Tests at 200 kg/cm ²	Page 106
Table III(B)7	Results of Pilot Plant Tests	Page 107
Figure 1(B)7	Yield and Material Balance (SV of 0.5)	Page 108
Figure 2(B)7	Yield and Material Balance (SV of 1.0)	Page 109

ENCLOSURE (B)7

SUMMARY

This project was established to determine the optimum operating conditions for production of aviation gasoline by high pressure hydrocracking of pine root oil. Pilot plant tests were essentially completed and the process was ready for large scale development to increase the supply of high octane aviation gasoline. These experiments were made on a pine root oil cut of 185-300°C in a small continuous pilot plant, using $MnO_3 + NiO$ catalyst, under reaction conditions of 0.15-1.0 space velocity, hydrogen pressure of 200 kg/cm² and temperature of 400-450°C. An aviation gasoline, with a 95 octane number (with 0.15% of Tetra Ethyl Lead), was obtained in yield of about 50% when SV was 0.5, and 28-30% when SV was 1.0.

I. INTRODUCTIONA. History of Project

The investigation of pine root oil as a source of aviation gasoline started at the end of 1944 as a result of the urgent demands of the war. Since satisfactory aviation fuel could not be obtained directly from the product of dry distillation of pine roots, refining methods of high pressure hydrocracking and catalytic cracking were investigated. For the hydrocracking studies described in this report, the oil fraction boiling from 185-300°C, obtained by dry distillation of pine roots, was used as raw material. (The fraction, boiling below 185°C was treated by simple catalytic reforming.) Since very few large scale hydrocracking plants were installed in Japan, these experiments were carried forward with great speed. Pine root oil has many special characteristics, for example, high content of acidic matter and resins, and it was most important to determine the operating conditions for a smooth working process, especially to find a strong and active catalyst with long life. It was expected that a high octane aviation gasoline composed of naphthenic or paraffinic hydrocarbons, would be obtained by the hydrocracking of pine root oil.

B. Research Personnel Working on Project

Chem. Eng. Lt. Comdr. R. YUMEN
Chem. Eng. Lt. Comdr. T. IIJIMA
Chem. Eng. Lieut. K. SONE
Chem. Eng. Lieut. S. INABA

II. DETAILED DESCRIPTIONA. Description of Test Apparatus

Studies were first made in small rotating autoclave to determine the proper conditions for hydrocracking of pine root oil, and finally continuous tests were made in a small scale pilot plant with a 3-10 liters reaction chamber. This plant is described by Chem. Eng. Lieut. K. SONE in his "Study on Hydrocracking of High Temperature Coal Tar".

B. Properties of Raw Material

Pine root oil boiling at 185-300°C, with a brownish-black color, was used as raw material. Properties of this stock are given below:

ENCLOSURE (B)7

Specific Gravity (d_{4}^{15})	0.9495
I.B.P. (°C)	165
10%	184
20%	192
30%	203
40%	215
50%	234
60%	262
70%	288
80%	299
90%	331
Final	332
Acidic Substance (% determined with 10% NaOH solution)...	24.4

C. Reaction Conditions

First, it was established by many tests in small autoclaves (five liters capacity); that the best conditions for the reaction were a temperature of 420-450°C and a hydrogen pressure of 200 kg/cm², using either Nickel and Molybdenum Oxide (NiO + MoO₃) or Molybdenum Sulphide (MoS₃) catalyst, refer to Tables I(B)7 and II(B)7. Although the latter catalyst was better from the standpoint of octane number, the former had a longer period of activity, since the sulphur in MoS₃ catalyst escaped within a few days, resulting in loss of activity. Under the condition of 100 kg/cm² of hydrogen pressure, the products were not satisfactory for aviation gasoline, having a comparatively high content of acidic substances (Table I(B)7). By increasing the pressure to 200 kg/cm², the properties of products changed rapidly and very superior aviation gasoline was obtained, with 95 octane number and almost no content of acidic substance. The yield of aviation gasoline was about 70% of total cracked product, and 50% of the raw material in the autoclave tests. In pilot plant tests, the yield was about 50% of the product, and about 40% of the raw material for a space velocity of 0.5. When SV was increased to 1.0, the yield dropped to 33% of the product, and 28% of the raw material. (Refer to Tables I(B)7, II(B)7, and III(B)7.)

The procedure for the pilot plant test was as follows. First, the hydrogen pressure was increased gradually by the compressor, until the pressure of the apparatus,--Reaction Chamber, Preheater, High Pressure Separator, Pipes, etc.--reached 200 kg/cm². The reaction chamber temperature was brought to 300°C by electric heating, and oil was gradually charged. After about six hours, 400°C temperature used in the first run was reached. The temperature was raised as slowly as possible to 470°C, which was the maximum temperature for this type apparatus, in order to maintain catalyst activity for one-two months at least. The experimental results (Table III(B)7) were regarded as a satisfactory basis for large scale plant operations at the Second or Third Naval Fuel Depot.

D. Yield and material balance for pilot plant test are given in Figure 1(B)7 and Figure 2(B)7.

E. It is understood that a large scale plant performance test in July 1945 at the Third Naval Fuel Depot showed almost the same results as obtained in these pilot plant experiments. It was said that in this plant test aviation gasoline with 91 octane number was obtained in yield of about 50% of pine root oil charged. This test only lasted for one-two weeks. Longer periods of operation were planned, however, to assist in meeting the great demand for aviation fuel in Japan.

ENCLOSURE (B)7

III. CONCLUSIONS

High pressure hydrocracking is one of the best methods for obtaining high octane aviation gasoline from pine root oil. However, since very few large hydrocracking plants were installed in Japan, simpler catalytic reforming methods were also to be adopted, though producing less satisfactory products. None of these methods actually resulted in large scale production of aviation gasoline from pine root oil, however. It has been definitely shown that an aviation gasoline of 91-95 octane number (with 0.15% of lead) can be produced in yield of about 50% from pine root oil by means of high pressure hydrocracking. Optimum reaction conditions are hydrogen pressure 200 kg/cm², temperature 400 to 450°C, space velocity 0.5-1.0 and using Nickel and Molybdenum (NiO + MoO₃) as catalyst. In the case of Molybdenum Sulphide (MoS₃), further investigation is necessary with regard to prolonging catalyst life.

Table I(B)7
RESULTS OF AUTOCLAVE TESTS AT 100 kg/cm²

		Experiment No.	
		1	2
Catalyst		NiO ₄ + MoO ₃	MoS ₃
Reaction Conditions	Hydrogen Pressure (kg/cm ²) Temperature (°C) Time (hr)	100 350 3	100 350 5
Products	Absorbed Hydrogen (wt % of Raw Oil) Yield of Cracked Oil (wt% of Raw Oil) Yield of Water (wt % of Raw Oil) Acidic Matter (vol % in Cracked Oil) Specific Gravity of Cracked Oil (d ₄ ¹⁵) I.B.P. of Cracked Oil (°C) 10% 50% 90% 97% Final	2.3 81.9 6.0 7.0 0.846 88 153 177 270 280 283	2.3 83.4 7.1 6.0 0.832 46 94 154 224 274 315
	Yield to	150°C Fraction (vol %) 160°C Fraction (vol %) 170°C Fraction (vol %) 200°C Fraction (vol %)	3 21 36 72
Aviation Gasoline Cut	Yield from Cracked Oil (vol %)	7.0	42.0
Octane No. of Aviation Gasoline	Clear With 0.15% of Lead	76.0 93.6	75.0 94.0

ENCLOSURE (B)7

Table II(B)7
RESULTS OF AUTOCLAVE TESTS AT 200 kg/cm²

		Experiment No.	
		1	2
Catalyst		NiO + MoO ₃	MoS ₃
Reaction Conditions	Hydrogen Pressure (kg/cm ²) Temperature (°C) Time (hr)	200 450 3	200 450 3
Products	Absorbed Hydrogen (wt % of Raw Oil) Yield of Cracked Oil (wt % of Raw Oil) Water (wt % of Raw Oil) Acidic Matter (vol % in Cracked Oil) Specific Gravity of Cracked Oil (d ₄ ¹⁵) I.B.P. of Cracked Oil (°C) 10% 50% 90% 97% Final Yield 150°C Fraction (vol %) to 160°C Fraction (vol %) 170°C Fraction (vol %) 200°C Fraction (vol %)	4.14 76 6.8 0.4 0.812 48 86 130 220 264 293 64 75 69 36	4.1 74 8.34 0.6 0.7646 20 63.5 120 185 210 230 73 85 79 94
Aviation Gasoline Cut	Yield from Cracked Oil (vol %) Acidic Matter in Aviation Gasoline (vol %) Specific Gravity (d ₄ ¹⁵) I.B.P. (°C) 10% 50% 90% 97% Final	70 0 0.804 62 94 117 147 160 170.4	87 0 0.7616 23.4 62.5 104.5 147.5 165.5 168.0
Composition of Aviation Gasoline	Unsaturate Hydrocarbon (vol %) Aromatic (vol %) Naphthenic Paraffinic Aniline Point (°C)	3.0 31.3 51.4 24.3 49.5	0 24.0 30.4 35.6 58.0
Octane No. of Aviation Gasoline	Clear With 0.15% of Lead	80.6 95.7	78.0 96.7

ENCLOSURE (B)7

Table III(B)7
RESULTS OF PILOT PLANT TESTS*

Catalyst	Experiment No.				
	1	2	3	4	5
	H ₂ O + MeO ₃	NiO + MeO ₃	NiO + MeO ₃	NiO + MeO ₃	NiO + MeO ₃
Reaction Conditions	200 420 430 450 460	200 430 450 470 480	200 430 450 470 480	200 430 450 470 480	200 430 450 470 480
Hydrogen Pressure (kg/cm ²)	6.0	4.3	5.0	3.9	4.8
Temperature (°C)	89.5	85.5	93.4	86.7	92.0
Space Velocity (Liquid Oil)	73.8	71.0	75.2	86.7	80.0
Space Velocity (Gas)	0.1	5.0	5.0	2.9	4.1
Charged Oil (lit/hr)	0.755	0.782	0.778	0.80	0.839
Charged Hydrogen Gas (m ³ /hr)	23.0	30.5	29	31	26
Run Length (hr)	71.5	77	78	91.5	100
Absorbed Hydrogen (wt % of Charged Oil)	10%	14.2	15.6	15.7	15.4
Yield of Cracked Oil (vol % of Charged Oil)	23.6	19.5	20.3	21.1	27.3
Water in Cracked Oil (wt %)	97%	286	287	318	273
Acidic Matter in Cracked Oil (vol %)	297	286	295	318	339
Specific Gravity of Cracked Oil (d ₄ ²⁰)	0	0.2	0.3	0.1	0.2
I.B.P. of Cracked Oil (°C)	0.2	0.3	0.5	0.2	0.2
10%	0.9	0.9	0.9	0.2	0.6
20%	0.1	0.4	0.6	0.3	0.6
50%	0.1	1.8	9.82	6.7	17.7
97%	85.0	78.2	86.42	90.2	74.9
Final	5.9	3.5	1.96	1.3	5.8
CO ₂ (vol %)	0.2	0.2	0.3	0.1	0.2
O ₂	0.2	0.3	0.5	0.2	0.2
C ₂ H ₆	0.9	0.9	0.6	0.3	0.6
CO	0.1	0.4	0.6	0.3	0.6
C ₂ H ₄	7.9	18.2	9.82	6.7	17.7
H ₂	85.0	78.2	86.42	90.2	74.9
n (Carbon Number)	5.9	3.5	1.96	1.3	5.8
	0.9	0.9	0.6	0.3	0.6
Specific Gravity (d ₄ ²⁰)	0.7727	0.7567	0.7463	0.7717	0.7438
Yield from Cracked Oil (wt %)	45.3	51.4	47.6	40.0	35.0
10%	34.0	30.2	26.0	34.0	36.0
50%	65.0	60.0	59.0	70.5	65.0
90%	112.5	107	117	110	115
97%	159	158	160	157	158
Final	170	169	173	170	170
Acidic Matter in Aviation Gasoline (vol %)	180	185	209	207	182
0	0	0	0	0	0
Unsaturated Hydrocarbon (vol %)	1.5	1.5	3.0	1.0	1.2
Aromatic	12.6	13.8	20.0	11.9	12.3
Naphthenic	40.6	59.0	40.5	56.9	54.2
Paraffinic	43.9	25.7	36.5	30.2	32.3
Aniline Point (°C)	49.1	55.6	54.2	50.2	53.0
Clear	75.5	76.0	72.5	78.1	78.5
With 0.1% of Lead	96.2	97.6	92.0	96.6	95.4

*Recycle oil used as raw material

ENCLOSURE (B)7

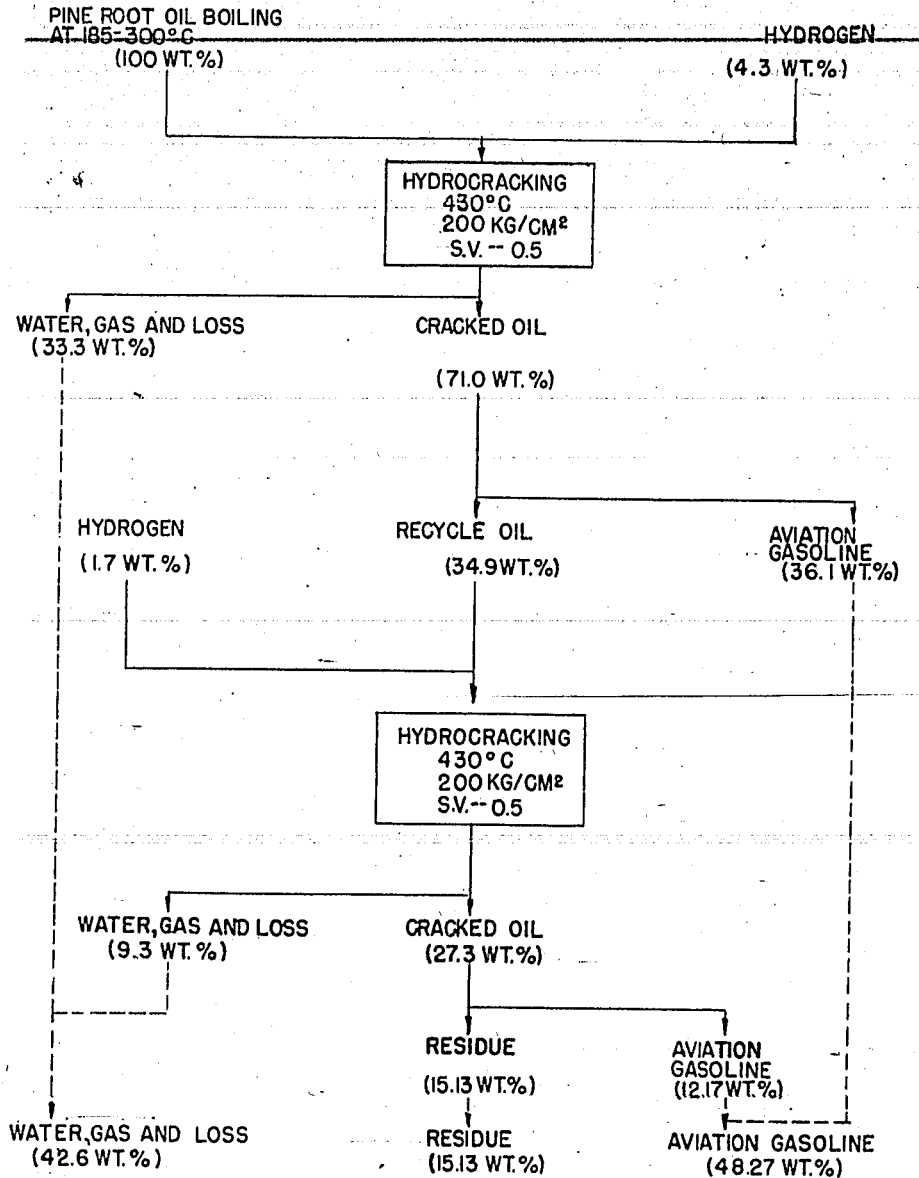


Figure 1(B)7
YIELD AND MATERIAL BALANCE
(S.V. of 0.5)

ENCLOSURE (B)7

YIELD AND MATERIAL BALANCE
(S.V. OF 1.0)

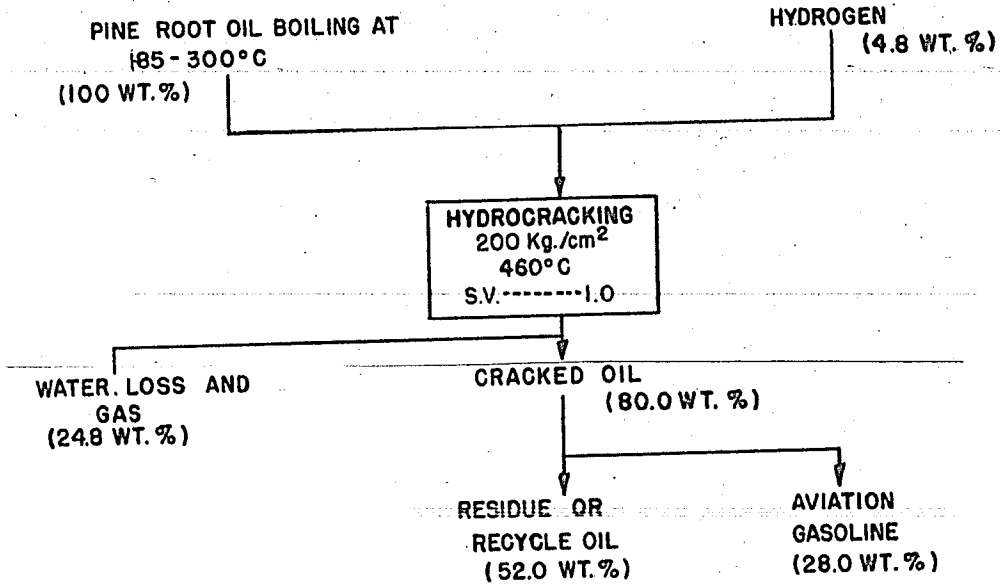


Figure 2(B)7
YIELD AND MATERIAL BALANCE
(S.V. of 1.0)